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Spectroscopic Determination of the Protonation and Oxidation States of 2,5-Dimercapto-1,3,4-thiadiazole

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Spectroscopic Determination of the Protonation and Oxidation States of 2,5-Dimercapto-1,3,4-Thiadiazole

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Abstract: The dimercaptan 2,5-dimercapto-1,3,4-thiadiazole (DMcT) has been examined widely as a component in secondary lithium battery cathodes. However, spectroscopic studies of its behavior have been impeded by general uncertainty regarding its vibrational band character. Therefore, assignment of the structure and vibrational bands for DMcT and some derivatives is reported in this contribution. The purpose of this study is to provide a basis for the unambiguous determination of protonation and oxidation state of DMcT.

In order to establish chemical bonding for cases where exocyclic thioamide groups could adopt either thiol or thione character, solution and solid state ^{13}C nuclear magnetic resonance spectroscopies have been employed (in conjunction with infrared and Raman spectroscopies). Using the bonding determined, primary chemical bond contributors have been assigned, when possible, to vibrational bands observed in the infrared and Raman spectra of these compounds in the solid state. In order to make such assignments, the observed bands for a series of systematically derivatized rings have been correlated with chemical bonding, spectra of the deuterated species, and literature reports.

The result is that herein is provided a resource of detailed spectroscopic data which is potentially useful to the study of this family of compounds in any context. Furthermore, several structural and spectroscopic assignments are intrinsically interesting, including: 1) the suggestion that the thioamide-containing compounds adopt the thione tautomer structure whenever the opposite nitrogen is unsubstituted; and 2) the assignment of an A_1 ring mode for the first time for this family of heterocyclic rings.

Introduction

The dimercaptan 2,5-dimercapto-1,3,4-thiadiazole (DMcT) (Scheme 1) has been successfully employed as an active component in composite cathode materials for use in secondary lithium batteries.¹⁻¹⁴ However, while several vibrational studies of DMcT and related compounds exist in the literature,¹⁵⁻¹⁹ a survey of structural assignments based on the vibrational band data in those reports reveals many inconsistencies (*vide infra*). This is due in large part to the complications introduced into the spectroscopy as a result of the thiol/thione tautomerization which is possible for the thioamide groups in DMcT and some of its derivatives^{15a,16b,c,17-31} (Scheme 2). As well, the spectroscopic signature of DMcT and its derivatives (Scheme 1) is complicated by simultaneous vibrational coupling between bands of similar frequency (especially those involving thione moieties) and extensive delocalization of electron density in the heterocycle due to the large number of possible resonance structures.²⁰ Together, these characteristics result in the experimental

observation of coupled and/or combination bands at uncommon frequencies.

Notwithstanding a continuing interest in DMcT,³²⁻⁴³ few data regarding its fundamental chemical and electrochemical reactivity are available. For this reason, several groups have recently concentrated on fairly fundamental studies of the properties of this compound using cyclic^{7,45,46} and rotating disk^{45d} voltammetries, electronic spectroscopy,^{45c,47} and quartz crystal microgravimetry.^{6,47}

While interest in this area has been directed toward characterizing the redox behavior of DMcT in dilute non-aqueous solutions, the complexity of its spectra and the inconsistencies between previous studies have prompted us to investigate first the structure of DMcT and derivatives in the solid phase. A brief communication on this topic is available.⁴⁸

In this report, the experimentally observed vibrational bands are assigned to their primary contributing bonds through the combined use of systematic chemical derivatization of DMcT and deuteration of certain derivatives, correlated with a survey of published results. Specifically, we have performed Fourier transform-NMR cross-polarization magic angle spinning (CPMAS), -infrared (FT-IR), and -Raman spectroscopic studies of solid samples of DMcT, the lithium salts of its two conjugate base forms, its dimer and polymer forms, and two methyl derivatives. The observed ¹³C resonances have been assigned using proton coupling for McMT in concentrated solution, as has been done previously for molecules similar to DMcT.²⁷ The results agree with previously reported crystallographic and NMR data.^{16b,31,39a,49} The vibrational modes have been assigned to molecular bands in a systematic fashion, beginning with the highest symmetry molecules, such as 2,5-dimethyl-1,3,4-thiadiazole (DMT), and progressing to the most structurally complicated molecules, such as the dimer form of DMcT. Furthermore, molecular structure has been correlated with observed spectral features in a way that is both reflective of the interesting, complex structure and chemistry of DMcT and its derivatives and useful as a diagnostic tool for further studies on systems including these compounds.

Experimental

Reagents

2,5-dimercapto-1,3,4-thiadiazole (DMcT), 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT), and 2,5-dimethyl-1,3,4-thiadiazole (DMT) were purchased from Tokyo Kasei Organic Chemicals and used without further purification. H₂O was doubly-distilled.

Methanol, hexanes, chloroform, lithium hydroxide monohydrate, iodine, and triethylamine (Kanto Chemical Co.) were used as purchased. Deuterated dimethylsulfoxide (Kanto Chemical Co.) was a NMR grade solvent. The dipotassium salt of DMcT, K_2DMcT , was purchased from Aldrich Chemical Co. (13,943-2, 98%) and used without further purification.

Synthesis

poly[dithio-2,5-(1,3,4-thiadiazole)] (poly(DMcT)) -- 2,5-dimercapto-1,3,4-thiadiazole (2.00 g, 13.3 mmol) was dissolved in a 1:1 H_2O :methanol solution (150 ml). A solution of I_2 (3.37 g, 13.3 mmol) in methanol (15 ml) was added dropwise, and a precipitate was observed almost immediately. The reaction mixture was stirred for 24 h under N_2 atmosphere, with gentle heating (40-50 °C) during the latter 8 hours. The precipitate was filtered and the light brown solid was washed with copious amounts of hexanes, methanol, and water and dried under vacuum at 70 °C for 12 h to leave a light yellow solid. Anal. Calc'd. for $C_2N_2S_3$: C, 16.21; N, 18.9; S 64.89. Found: C, 16.19; N, 19.01; S, 64.75.

di-lithium salt of 2,5-dimercapto-1,3,4-thiadiazole (Li_2DMcT) -- This compound was prepared similarly to procedures detailed elsewhere.^{45b,45c} Briefly, an equivalent of DMcT was added to an aqueous solution containing two equivalents of $LiOH \cdot H_2O$. The water was removed directly from the light yellow solid via rotary evaporation. Elemental analysis of the product shows that Li_2DMcT prepared in this way is more accurately written $Li_2DMcT \cdot 2H_2O$: Anal. Calc'd. for $C_2H_4N_2O_2S_3Li_2$: C, 12.12; H, 2.02; N, 14.14; O, 16.15; S, 48.56; Li, 7.01. Found: C, 12.27; H, 2.19; N, 13.91; S, 48.31; Li, 6.86.

bis(2-methyl-1,3,4-thiadiazoyl)-5,5'-disulfane (dimer McMT) -- A 200 ml round bottom flask was charged with chloroform (10 ml), 2-mercapto-5-methyl-1,3,4-thiadiazole (2.0 g, 15.2 mmol) and triethylamine (1.55 g, 15.3 mmol). To the reaction mixture was added iodine (1.93 g, 7.6 mmol) in chloroform (20 ml) over a period of 10 min. with vigorous stirring. The reaction was continued for 1 h under N_2 , during which time the solution became pale yellow. The solution was extracted with water, dried over anhydrous sodium sulfate, and the solvent was evaporated. After recrystallization from methanol, a highly crystalline white solid was obtained (1.69 g, 85 % yield). 1H -NMR (300 MHz, ppm, $DMSO-d_6$) δ 2.74 (methyl 3H). ^{13}C -NMR (300 MHz, ppm, $DMSO-d_6$) δ 165.2, 169.4 (thiadiazole C), δ 15.5 (methyl C). Anal. Calc'd. for $C_6H_6N_4S_4$: C, 27.44; H, 2.3; N, 21.35; S, 48.88. Found: C, 27.40; H, 2.5; N, 21.35; S, 48.54.

mono-lithium salt of 2,5-dimercapto-1,3,4-thiadiazole (LiDMcT) -- This compound was prepared similarly to procedures detailed elsewhere.^{45b,45c} Briefly, an equivalent of DMcT was added to an aqueous solution containing one equivalent of LiOH·H₂O. The water was removed via rotary evaporation to give an orange to red solid. Elemental analysis indicates that LiDMcT is more accurately written LiDMcT·1.5H₂O: Anal. Calc'd. for C₂H₄N₂O_{1.5}S₃Li: C, 13.11; H, 2.21; N, 15.29; O, 13.10; S, 52.50; Li, 3.79. Found: C, 13.30; H, 2.12; N, 15.30; S, 52.67; Li, 3.75.

bis(2-mercapto-1,3,4-thiadiazoyl)-5,5'-disulfane (dimer DMcT) -- To 500 ml nitrogen-purged H₂O was added 0.45 g (3 mmol) DMcT and 0.68 g (3 mmol) K₂DMcT, in that order. After the solids were completely dissolved, the solution was made ca. 1 M in H₂SO₄. To this solution was added dropwise a solution of 2.4 g (6 mmol) Ce(SO₄)₂·4H₂O in 300 ml of 1 M aqueous H₂SO₄ (nitrogen-purged) under flowing nitrogen gas. The immediate yellow precipitate was filtered under flowing nitrogen, recrystallized from methanol, and dried overnight under vacuum. UV/Vis: λ_{max} 329 nm ($\epsilon \approx 17,000$). Anal. Calc'd for C₄H₂S₆N₄: C, 16.10; H, 0.68; N, 18.77; S, 64.46. Found: C, 16.12; H, 0.54; N, 18.60; S, 60.5. Deuteration of this compound was accomplished by dissolution of 150 mg dimer DMcT in 50 ml d₆-acetone (Merck, 13,369, 99.5%) and 5 ml d₁-chloroform (E. Merck, 2446, 99.95%). To that solution was added 50 ml D₂O (Isotech, Inc., 82-70001, 99.9%). All three solvents were purged with nitrogen or argon before and during the reaction. The mixture was vigorously stirred for ca. 20 minutes, then the solvents were removed by rotary evaporation and the resultant yellow solid was dried under vacuum.

Spectroscopy

All spectra were recorded at room temperature.

NMR -- Solid-state spectra were recorded using a 400 MHz JEOL (GX-400) instrument and represent proton-uncoupled states. ¹³C spectra shown represent 1118 (DMcT) or 504 (McMT) averaged scans. The pulse delay was 10 seconds for the DMcT spectrum.

The ¹³C solution phase spectrum of McMT (in DMSO-d₆) was recorded using a 300 MHz JEOL (JNM-LA300) instrument and represents the proton-coupled state (proton irradiation was not used). The spectrum shown represents 112 averaged scans.

FT-Raman -- Spectroscopy was performed using a Bio-Rad 60 FTS/896 instrument equipped with a Raman attachment, a Ge detector, and a quartz beamsplitter. Excitation

radiation (0.46 to 0.48 W at 1064 nm) was provided by a Nd:YAG laser (Spectra-Physics, model T10-106c). Samples were packed into capillary or NMR tubes. Spectra represent 1024 co-added scans taken at 4 cm⁻¹ resolution, except the poly(DMcT) and dimer McMT spectra which represent 4096 co-added scans taken at 4 cm⁻¹ resolution. Data was singly zero-filled and a triangular apodization was used in calculation of the spectra.

FT-IR -- Spectroscopy was performed using a Bio-Rad 60 FTS/896 instrument equipped with a mercury-cadmium-telluride (MCT) detector and a KBr beamsplitter. Spectra represent 512 co-added scans taken at 2 cm⁻¹ resolution. Data was singly zero-filled and a triangular apodization was using in calculation of the spectra. Dry air purge included a gas-phase impurity, apparent in the IR spectra as a very sharp, variable peak at ca. 668 cm⁻¹. Liquid water in the samples is evidenced in the spectra by broad peaks of variable absorbance at 3300 and 1635 cm⁻¹. CO₂ in the sample compartment resulted in two characteristic peaks of variable intensity in the region 2300 to 2400 cm⁻¹. Samples were prepared by grinding the compounds in KBr powder (Jasco Parts Center, 722E) and pressing the mixture under vacuum.

Results

¹³C NMR Spectroscopy

Figure 1a shows the solid phase ¹³C spectra of DMcT and McMT. Proton coupling of McMT in concentrated (DMSO) solution has been examined in order to assign the observed resonances. The solution phase proton-coupled ¹³C spectrum of McMT is shown in Figure 1b. McMT shows three peaks at 17.3, 164.6, and 189.0 ppm in the solid phase (Figure 1a, top) and at 15.9, 159.5, and 188.4 ppm in the liquid phase (Figure 1b).

Assignment of these peaks can be made by consideration of the proton coupling for each of the two possible tautomers of this compound, which are shown in Scheme 2. For each of these tautomers, there are three types of carbons. Based on the large value of the proton coupling constant, the low-field peak at ca. 16 ppm in the solution phase spectrum (Figure 1b) is assigned to the carbon in the methyl group. The thioamide carbon attached to this methyl group is responsible for the peak at ca. 160 ppm based on the lower, but measureable, value of its proton coupling constant (Figure 1b, inset A). The remaining peak at 188 ppm, which exhibits no appreciable proton coupling, (Figure 1b, inset B) must derive from the other carbon. While the nature of this carbon (i.e. as a thione or

thiol carbon) cannot be unambiguously determined from these assignments, the upfield position of this peak is consistent with its being a thione carbon, in agreement with previous assignments for McMT, DMcT and related compounds.^{27,39a,49-52}

Based on these results, the solid phase spectrum (Figure 1a, top) is assigned in a similar manner, where the peak at 17.3 ppm represents the methyl carbon, the peak at 164.6 ppm represents the carbon bonded to the methyl group, and the peak at 189.0 ppm represents the carbon of the thioamide group, as shown in Scheme 3. Similar to the solution result, this group appears to be in the thione tautomer form. Taken together, these results show that for McMT, the predominant tautomer in the solid state is the thione form, in agreement with a previous report.^{16b}

The spectrum of solid DMcT (Figure 1a, bottom) shows two resonances at 160.2 and 189.5 ppm, which are assigned to the thiol and thione carbons, respectively, of the thiol/thione tautomer in Scheme 2. This assignment, depicted in Scheme 4, is based on the results for McMT detailed above as well as previous assignments.^{27,39a,49-52}

In view of published work,⁵³ it is reasonable to expect that the observed intensities of these proton-uncoupled ¹³C resonances are largely unaffected by the position of the hydrogen (i.e. either on the nitrogen or on the sulfur atom). Assuming that the resonance at ca. 160 ppm contains contributions from the thiol-bonded carbons in both the dithiol and thiol/thione tautomers, integration of these resonances indicates that the sample consists essentially entirely of the thiol/thione tautomer. This result is in agreement with a crystal structure by Bats,³¹ which showed only the thiol/thione tautomer in the single crystal sample.

Overall, these results suggest that 5-substituted 2-mercapto-1,3,4-thiadiazole rings exist in the thione tautomer form but that 4-substituted rings exist exclusively in the thiol tautomer form. Such bonding seems to have a significant effect on the reactivity of the thioamide groups, where those which are constrained to be in the thiol tautomer (such as DMcT) exhibit pK's in the -1 to -2 range,^{19b} while those which are free to assume the thione tautomer (such as McMT) have pK's of ca. 5 to 7.^{45b,52b}

Vibrational Spectra

IR and Raman spectra were obtained for DMcT and a number of different derivatives. These spectra are presented below. The objective of this part of the study was to allow for the unambiguous determination of the oxidation state and the state of protonation of the various compounds, in the context of their use in battery systems.¹⁻¹⁴

Thus, the assignments of these spectra are not complete. Rather, identification of those modes that are diagnostic of the redox and acid/base chemistry of these compounds has been of primary concern. Compounds with relatively simple spectra are presented first to facilitate the assignments.

DMT (see Scheme 1 for compound notations) is a highly symmetric molecule⁵⁴ which has been previously used as a model compound for NMR studies,⁵⁵ as a nitrification inhibitor in soil,⁵⁶ and as an antifoulant additive for high temperature hydrocarbon processing.⁵⁷ Its reactivity to several transition metal centers has been reported.^{16c,58}

Figure 2 shows the Raman (top) and IR (bottom) spectra for DMT. The region from ca. 3000-2700 cm^{-1} contains several weak bands that derive from C-H stretching, overtones, and Fermi resonances.^{59,60} In addition, several peaks appear in the region 1231-1140 cm^{-1} in the IR which are assigned to ring modes coupled to the (exocyclic) C-C stretch and a ring stretching mode (described in detail below). The former spectral region has not been analyzed in detail because it is not useful for distinguishing redox or acid/base chemistry.

The other relevant bands and their assignments are given in Table 1. The most prominent and diagnostically useful of these are the C=N stretches (where the asymmetric stretch, ν_{as} , and symmetric stretch, ν_{s} , have been assigned to the peaks at ca. 1481 and 1433 cm^{-1} , respectively, based on the skeletal vibrations for thiophene, pyrrole, and furan⁶¹) and the C-S-C stretches (where the ν_{as} and ν_{s} modes have been assigned to the peaks at ca. 777 and 658 cm^{-1} , respectively⁶²). These stretches are illustrated in Scheme 5 and 6, respectively. The strong coupling between the two C=N bonds is illustrated by the large splitting between the ν_{as} and ν_{s} modes. Assignment of the endocyclic C-S-C modes is further supported by the observation that those peaks are present in every spectrum reported here and are largely invariant in position. As well, the observed relative intensities of the asymmetric and symmetric modes are in agreement with IR/Raman selection rules.²¹ Finally, the N-N stretching mode of the ring has been assigned to the peak at 1066 cm^{-1} based on its presence in the Raman spectrum and results reported for hydrazine.⁶³

The polymer form of DMcT has been previously studied for use as a high-temperature battery cathode and fuel cell component.⁸⁻¹² Several synthetic routes for preparation of poly(DMcT) have been reported.^{8-12,64}

Figure 3 shows the spectra of poly(DMcT). The C=N band is observed at 1383 cm^{-1} in the Raman spectrum and at 1379 cm^{-1} in the IR spectrum. This difference in

frequency is less than the resolution of the FT-Raman spectrum, i.e. 4 cm^{-1} -- we return to this point below. Poly(DMcT) also shows the symmetric C-S-C stretch at 646 cm^{-1} and a band at 522 cm^{-1} which can be assigned to the S-S stretch, based on assignments for diphenyl disulfide⁶⁵ and other compounds.²¹ This latter band is thus a useful marker for the oxidation state of these materials. Also, a strong IR-absorbing band at 1047 cm^{-1} is assigned to an A_1 mode that is predominantly due to an out of phase combination of the N-N and symmetric C-S-C stretches, as depicted in Scheme 7. Modes of this type are frequently observed in the IR spectra of diene-like five membered rings, with thiophene, pyrrole and furan being the parent examples.⁶¹

The dibasic form of DMcT, $\text{Li}_2\text{DMcT}\cdot 2\text{H}_2\text{O}$, has also been studied for use as a component in both high-temperature and room-temperature battery systems.^{7-10,45,48}

Figure 4 shows the spectra of $\text{Li}_2\text{DMcT}\cdot 2\text{H}_2\text{O}$. The salient features include the C=N and C-S-C asymmetric and symmetric stretches and the N-N stretch. In addition, a strong band at 1068 cm^{-1} in the IR spectrum is assigned to the aforementioned A_1 mode depicted in Scheme 5. The fact that this sample is not contaminated with poly(DMcT) is shown by the lack of any disulfide stretching bands near 500 cm^{-1} . A broad band is observed centered around ca. 600 cm^{-1} due to the included water.

Note that in this set of spectra, the C=N symmetric and asymmetric stretching frequencies were split much less, i.e. 20 cm^{-1} , than in DMT, although DMT and $\text{Li}_2\text{DMcT}\cdot 2\text{H}_2\text{O}$ differ in structure only by the character of their exocyclic moieties. This observation is qualitatively similar to the C=N stretching character in the poly(DMcT) case. We have verified that this is an authentic trait of the dibasic form of DMcT by measuring the spectra of commercially available K_2DMcT . Those spectra had similar features, shifted slightly in position, with a splitting between the C=N coupled stretches of only 12 cm^{-1} . These results suggest that the single C=N band observed in the poly(DMcT) spectra could be attributed to both of the C=N bonds in its monomer units. In other words, they suggest that the C=N bonds do not vibrationally couple to a significant extent when the monomers are polymerized.

The spectra of the McMT disulfide dimer, dimer McMT, are shown in Figure 5. Notable features for this compound include the stretches from the C=N, N-N, C-S-C, and S-S groups. In addition, the IR spectrum shows several strong bands in the $1083\text{--}983\text{ cm}^{-1}$ range that were not observed for the other compounds. These bands have previously been attributed to coupling between the ring modes and the C-S bonds external to the ring in related compounds.⁶⁶ However, we can not discount the possibility that some could originate from the A_1 ring mode discussed above.

The methyl derivative of DMcT, McMT, has been studied and used in much the same context as DMcT (*vide supra*), especially in that McMT has been shown to coordinate many transition metal centers.^{16,58b,67} It has been shown above and previously reported^{16b} that McMT exists primarily as the thione tautomer (Scheme 2 and 3) in the solid state.

Thus, the vibrational spectra (shown in Figure 6) reflect the features expected for this structure. For example, the presence of the N-H bond is indicated by the N-H in-plane bend at ca. 1450 cm⁻¹ in both the IR and Raman spectra⁶⁸ and by the N-H torsional mode at 767 cm⁻¹ in the IR.^{16c,69,70} Further, only one C=N stretch is observed at ca. 1555 cm⁻¹. Finally, the band at ca. 1270 cm⁻¹ in both spectra can be assigned to the thioamide II mode,^{18d,70} which is generally assumed to be a combination of C-N and C=S stretching and N-H bending for acyclic thioamides.⁷⁰ However, in the case of these thiadiazole derivatives, the fact that this mode does not shift appreciably when complexation to a metal through the S atom occurs^{16b} or when the N-H group is deuterated^{16c} suggests that this mode is predominantly derived from the C-N stretch. This is qualitatively supported by the observation by Suzuki^{70a} that deuteration of thioacetamide reduces the N-H bending contribution to that band.

The bands from ca. 3200 to 2600 cm⁻¹ have also been assigned by Suzuki^{70b} (for the general thioamide case) to overtones of the thioamide group, stretching of the N-H bond, and Fermi resonances between those two modes. We have not assigned these peaks because they are not diagnostically useful due to the complexity of the mode coupling (although we note that, based on deuteration studies in our laboratory, the N-H stretching mode appears to be the primary contributor for the weak band observed at ca. 3200 cm⁻¹).

Note that the relative position in frequencies of the C=N stretch and the N-H bend observed for the McMT spectra is counter-intuitive to the general trend observed in DMcT, LiDMcT, and dimer DMcT (see below) as well as other cyclic thioamides.⁷¹ We have made this assignment based primarily on a deuterated spectrum reported by Peyronel and co-workers.^{16b,16c} In that study, the 1450 cm⁻¹ peak shifted by ca. 100 cm⁻¹ and the 763 cm⁻¹ peak by ca. 200 cm⁻¹ to lower energies upon deuteration while the peak at 1550 cm⁻¹ was largely unaffected, in agreement with an assignment by Edwards and co-workers.¹⁵

One additional point about these spectra concerns the modes associated with the C=S bond. Due to strong coupling between this bond and the ring system, the C=S stretch does not appear as an isolated band. Instead, it manifests itself by contributing to several bands in the range of 1200-600 cm⁻¹.^{71,72}

The monobasic form of DMcT has been isolated previously (as the pyridinium salt) for studies of its metal chelating ability.¹⁸ Its presence has been postulated to explain IR spectral results in studies of the metal bonding characteristics of DMcT⁷³ and to predict reactivity of DMcT to alkylation.^{49b}

The spectra of LiDMcT•1.5H₂O (i.e. the lithium salt of the monobasic form) are shown in Figure 7. Salient features include the N-H bend at 1503 cm⁻¹ in the IR, a single C=N stretch at 1405 cm⁻¹ which is present in both the IR and Raman spectra, the C-S-C asymmetric and symmetric stretches, and the thioamide II band at ca. 1300 cm⁻¹. Note that the C=N stretching frequencies in both this compound (1405 cm⁻¹) and the dianion of DMcT (1393, 1372 cm⁻¹) are quite low due to the electron donating character of the thiolate group. The band at 1482 cm⁻¹ is due to methanol⁶⁰ which is present as an impurity in the sample from the preparative route. Again, a broad band is seen around 600 cm⁻¹ due to the included water.

As discussed in the Introduction, DMcT has enjoyed considerable attention in a variety of contexts.^{1-17,18b-d,22,24-26,28,31-43,45-52} Assignment of its vibrational modes was driven historically by an interest in determining the tautomeric form(s) in which it exists in various environments. Unfortunately, since the seminal work by Thorn,^{19a} little agreement on these assignments is apparent in the literature. In the treatment here, we have relied primarily upon the results for the systematic derivatives of DMcT described above and upon the results of deuteration of DMcT.

Figure 8 shows the spectra of DMcT, which was shown to exist predominantly in the thiol/thione tautomer in the amorphous solid phase by ¹³C-NMR (*vide supra*) and in the single crystal by X-ray crystallography.³¹ The prominent bands are those due to the N-H bend and torsional mode (at ca. 1508 and 750 cm⁻¹, respectively), the single C=N stretch (at ca. 1450 cm⁻¹), the thioamide II band (at ca. 1275 cm⁻¹), and the C-S-C stretches.

Note that the weak peaks observed in the IR and Raman spectra at ca. 940 and 918 cm⁻¹ have been assigned to both the C-S-H in-plane bending modes¹⁵ and C=S stretching modes.¹⁶ While both assignments have merit,²¹ the positions of these peaks are strongly affected by coordination to a metal center through the thione sulfur^{16c} and not affected by deuteration of the compound.^{18d} Such results support the assignment of these peaks to modes of the C=S stretch. Finally, an especially important band for determining the tautomeric form and degree of protonation is the strong S-H stretch at 2483 cm⁻¹ in the both Raman and IR spectra.

The last compound which will be discussed is the disulfide dimer of DMcT. To our knowledge, only one other structural study has been reported on this molecule: reaction of molybdenum(V) with the DMcT monomer produced crystals of the oxidized dimer, devoid of molybdenum.²⁸ X-ray diffraction analysis of the crystals indicated that the two rings are not co-planar, that the thioamide groups both possess substantial thione character, and, furthermore, that the geometries in the two rings are significantly different.²⁸ That result has been verified and expanded upon in recent efforts by Shouji and Buttry^{45e} which have clearly identified the protons in dimer DMcT as being bonded to the nitrogen atoms.

Those characteristics are reflected in the spectra of the DMcT disulfide dimer, dimer DMcT, shown in Figure 9. The features of these spectra are entirely consistent with a primarily thione/thione dimer (i.e. both rings are mostly in the thione tautomeric form). This assignment is supported by the following observations: the strong N-H bends at ca. 1500 and 1388 cm^{-1} in both spectra, the thioamide II bands at ca. 1270 and 1215 cm^{-1} in both spectra, and an N-H torsion at 760 cm^{-1} in the IR.

An interesting feature of the spectra is the presence of two N-H bending bands, two C=N stretching bands (at 1474 and 1446 cm^{-1}), and two N-N stretching bands (at 1040 and 1020 cm^{-1}), rather than single bands as would be expected for the case of two thioamide groups in identical rings. Given the contrasting electronic character of the rings^{28,45e} and the sensitivity of these bands to the degree of electron donation demonstrated by the compounds discussed above, it is not surprising that two distinct sets of bands are observed.

Note that assignment of the N-H bends and C=N stretches were made by measuring the IR and Raman spectra of the deuterated dimer (included as supplementary material), in which the N-H bends are shifted to 1351 and 1307 cm^{-1} and the C=N stretches have remained largely invariant at 1466 and 1452 cm^{-1} . Also, the thioamide II bands are decreased in frequency, while the lower energy bands not associated with endgroup modes are not significantly shifted.

Finally, assignment of the S-S stretching mode to the bands at 544 and 532 cm^{-1} has been made with some reservation. Assignment of such modes is typically complicated by both rotational isomerization around the S-S bond and interfering bands in this region.^{65,74} While any of the bands at 544, 532, or 488 cm^{-1} could conceivably originate from the S-S stretching mode,^{65,74} the doublet structure of the bands at 544 and 532 cm^{-1} is reminiscent of the band structures typical of other disulfide bonds.⁷⁴ Based on this implication, and the fact that the S-S stretch is observed in the 535-550 cm^{-1} range for poly(DMcT) and dimer McMT, the S-S stretching mode has been assigned to the peaks at 544 and 532 cm^{-1} . In the future, we hope to study how the extent of

oligomerization affects the S-S stretching frequencies for these compounds.

Discussion

Several spectroscopic results of this study are intrinsically interesting. First, the A_1 lowest frequency ring mode shown in Scheme 7 has been assigned (e.g. at 1210 cm^{-1} in DMT, at 1047 cm^{-1} in poly(DMcT) and at 1068 cm^{-1} in the $\text{Li}_2\text{DMcT}\cdot 2\text{H}_2\text{O}$) for the first time for the thiadiazole ring. These modes are at quite low frequencies in these systems compared to their frequencies in the pyrrole and furan systems (e.g. $1450\text{--}1350\text{ cm}^{-1}$) due to contributions to the displacement from the endocyclic sulfur and nitrogens and, except in the DMT case, exocyclic sulfurs.

Second, several previous studies¹⁵⁻¹⁹ emphasized the use of the N-H stretching modes to identify the presence of thione tautomers, although, as shown by Suzuki,⁷⁰ this practice is greatly complicated by the presence of overtones and Fermi resonances in that region. In the spectra reported herein, we can observe characteristic (although complex) bands in the N-H stretching region when thione tautomers are present, i.e. in the McMT, $\text{LiDMcT}\cdot 1.5\text{H}_2\text{O}$, DMcT, and dimer DMcT spectra. Such an assignment is further supported by the absence of such bands in the spectra of compounds which cannot adopt a thione tautomer form.^{42b} However, from the assignments made in this report, it appears more straightforward to use the N-H bending and torsional modes to identify the character of such tautomers. Thus, the tautomerization equilibria and oxidation states for these compounds are reflected most clearly in the N-H bending and torsional bands in combination with the C=N stretching bands, and not in the N-H stretching bands.

Third, a relatively strong thioamide band is observed in both the IR and Raman spectra at ca. 1275 cm^{-1} . This band is characteristic of thione groups,^{18,70} and thus can be used to diagnose the presence of thione tautomers in McMT, $\text{LiDMcT}\cdot 1.5\text{H}_2\text{O}$, DMcT and the disulfide dimer of DMcT. Our results and the results of other investigators who have studied similar compounds^{16b,16c} suggest that for these compounds this mode is predominantly derived from C-N stretching.

Fourth, it is apparent from a comparison of the poly(DMcT) and dimer DMcT spectra (in Figures 3 and 9, respectively) that careful differentiation of these compounds is quite difficult using Raman or IR spectroscopy. In particular, the IR bands of poly(DMcT) overlap significantly with those of the dimer. Thus, the presence of trace polymer in samples of dimer would not be obvious from an IR spectral analysis. However, the N-N and S-S stretching bands at 1085 and 522 cm^{-1} in the Raman spectrum of the polymer are distinctly separate from any dimer bands. Thus, Raman spectroscopy (when excited with 1064 nm radiation) appears to be more useful than IR

spectroscopy when monitoring oxidation states of dimer or oligomer DMcT.

Last, these results are entirely consistent with the notion that the predominant form of all of these compounds is the thione tautomer when the opposite nitrogen is unsubstituted, and therefore is in agreement with the previous spectral and X-ray crystallographic studies of these compounds. In future contributions, we will examine the issue of tautomerization in solution and in the composite secondary cathode films formed with DMcT and poly(aniline).

A major outcome of this study is that the spectral characteristics of these compounds provide a relatively comprehensive basis from which to unambiguously determine both the oxidation state and the degree of protonation of DMcT and its derivatives. The fact that vibrational spectroscopy can be employed for this purpose is particularly attractive because of its ease of use as an *in situ* tool in electrochemical studies.⁷⁴ Thus, the present work will serve as a prelude to a thorough *in situ* vibrational spectroscopic study of the redox and acid/base behavior of the DMcT/poly(aniline) lithium secondary cathode system. It will be essential learn how the redox processes of these cathodes depend on protonation and oxidation state in order to tailor the system for optimal performance. This effort will require a careful accounting of the species within the films, a task that should be possible now given the detailed spectroscopic information that is available on the DMcT system (*vide supra*) and on poly(aniline).⁷⁵

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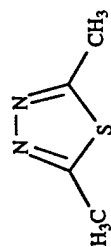
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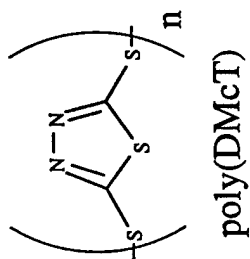
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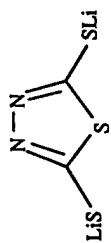
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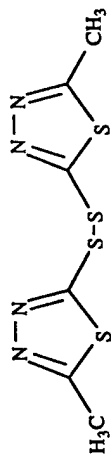
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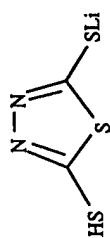
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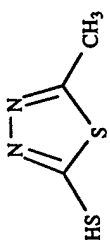
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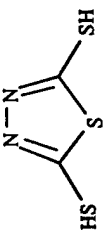
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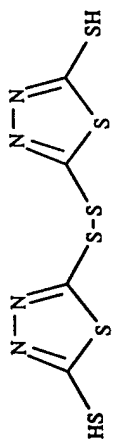
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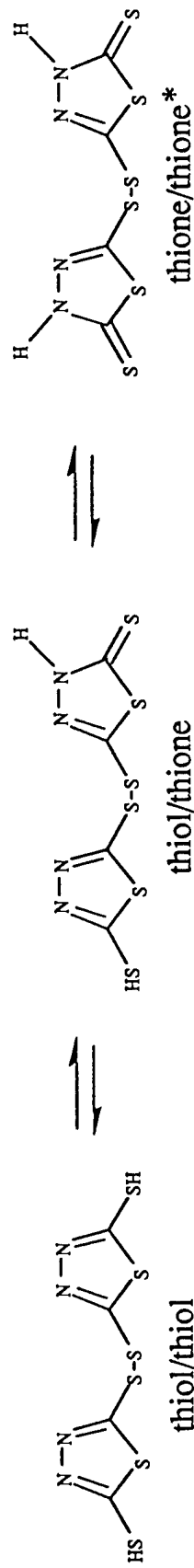
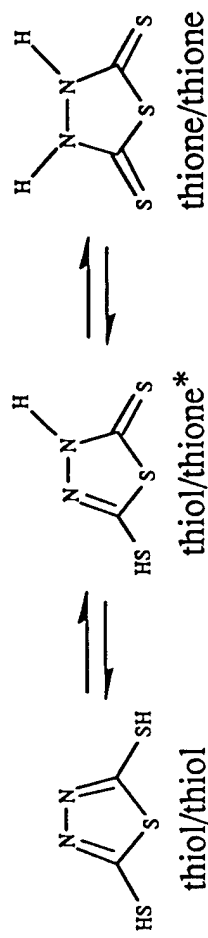
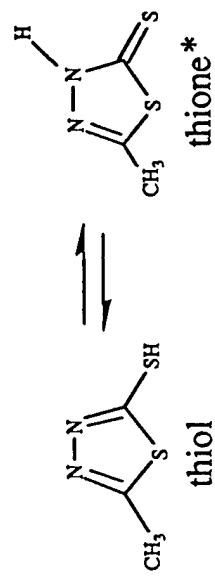
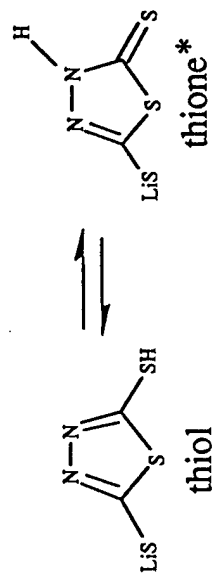
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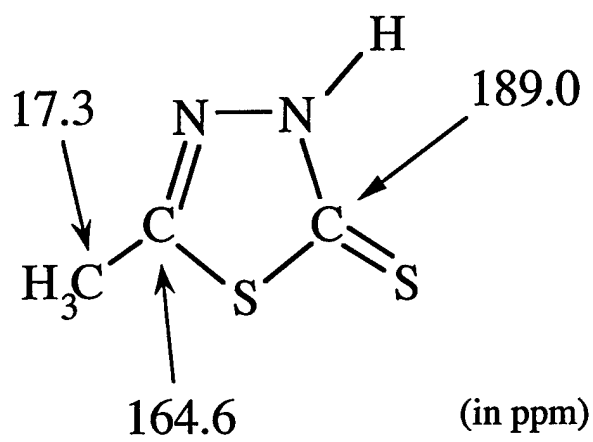
DMcT



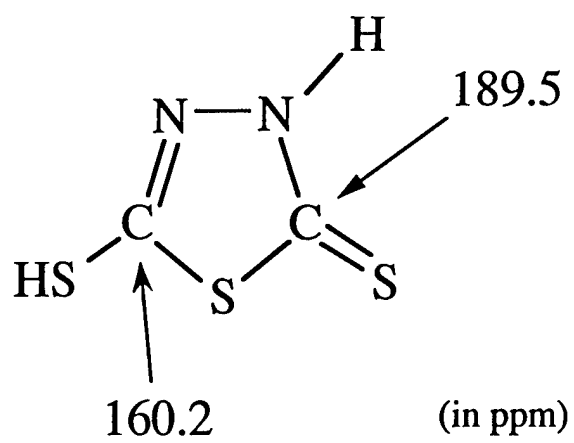
dimer DMcT



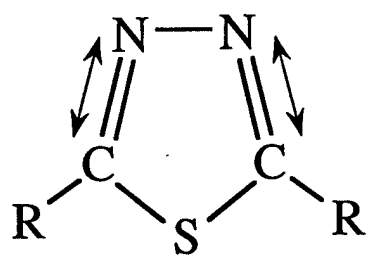
* = primary tautomer form in the solid phase



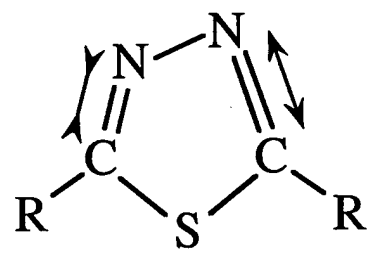
Reo et. al. Scheme 3



Scheuch

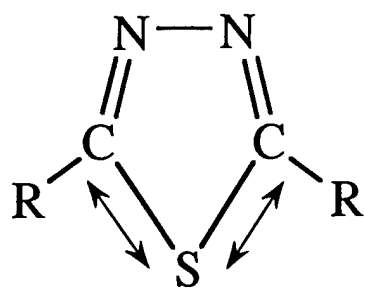


symmetric C=N stretch

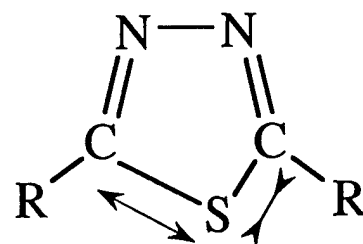


asymmetric C=N stretch

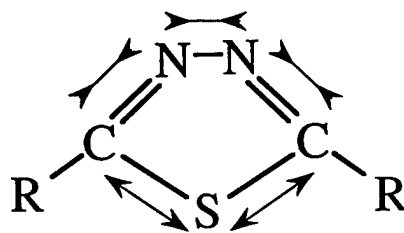
Scheme 5



symmetric C-S-C stretch



asymmetric C-S-C stretch



A₁ ring stretch

Figure Captions:

Figure 1: a) CPMAS NMR spectra of powder samples of McMT (top) and DMcT (bottom).

b.) Solution ^{13}C NMR spectrum of McMT in DMSO-d_6 . Insets A and B show the proton coupling in the two downfield peaks.

Figure 2: Raman (top) and IR absorbance (bottom) spectra of DMT.

Figure 3: Raman (top) and IR absorbance (bottom) spectra of poly(DMcT).

Figure 4: Raman (top) and IR absorbance (bottom) spectra of Li_2DMcT .

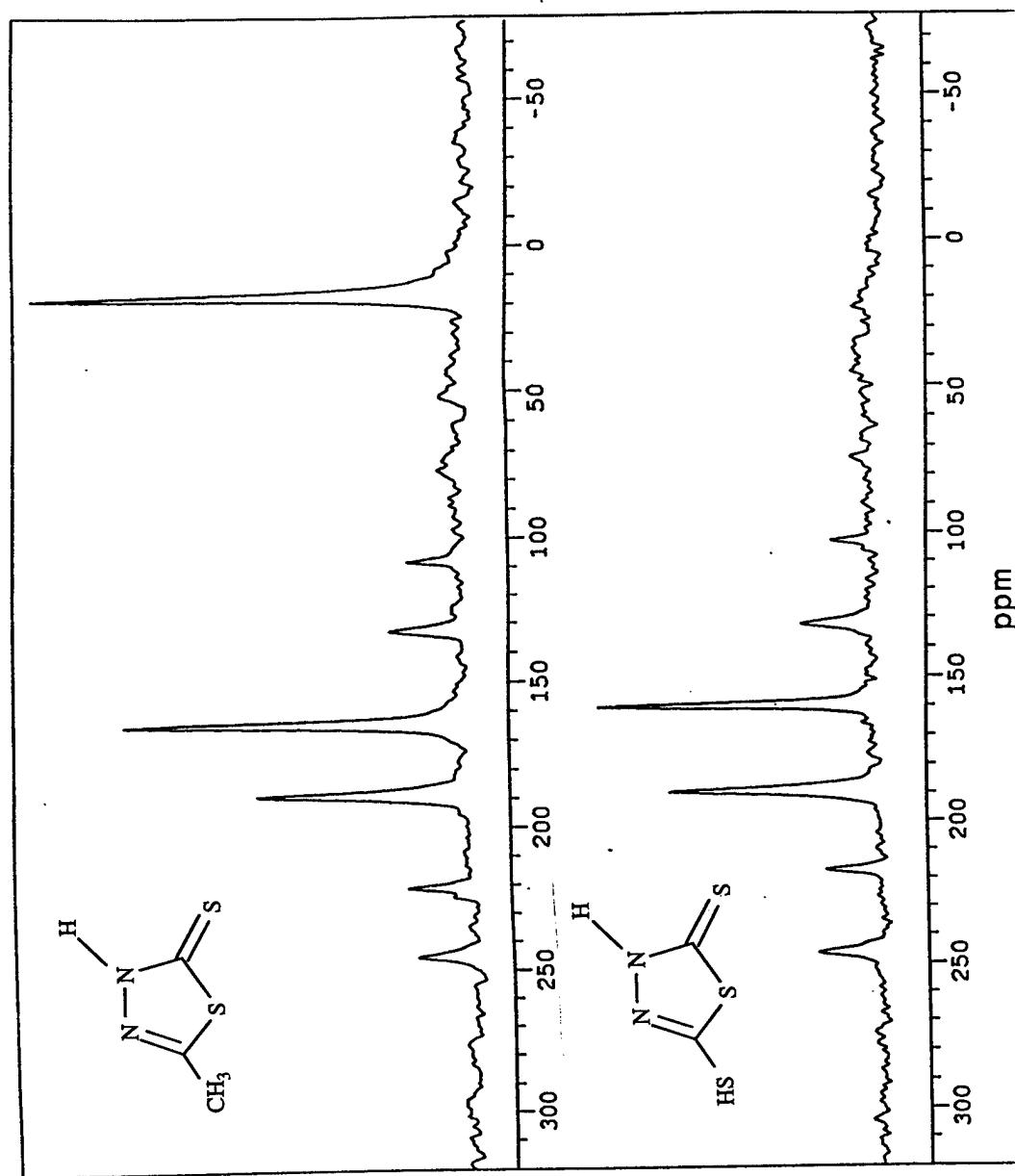
Figure 5: Raman (top) and IR absorbance (bottom) spectra of dimer McMT.

Figure 6: Raman (top) and IR absorbance (bottom) spectra of McMT.

Figure 7: Raman (top) and IR absorbance (bottom) spectra of LiDMcT .

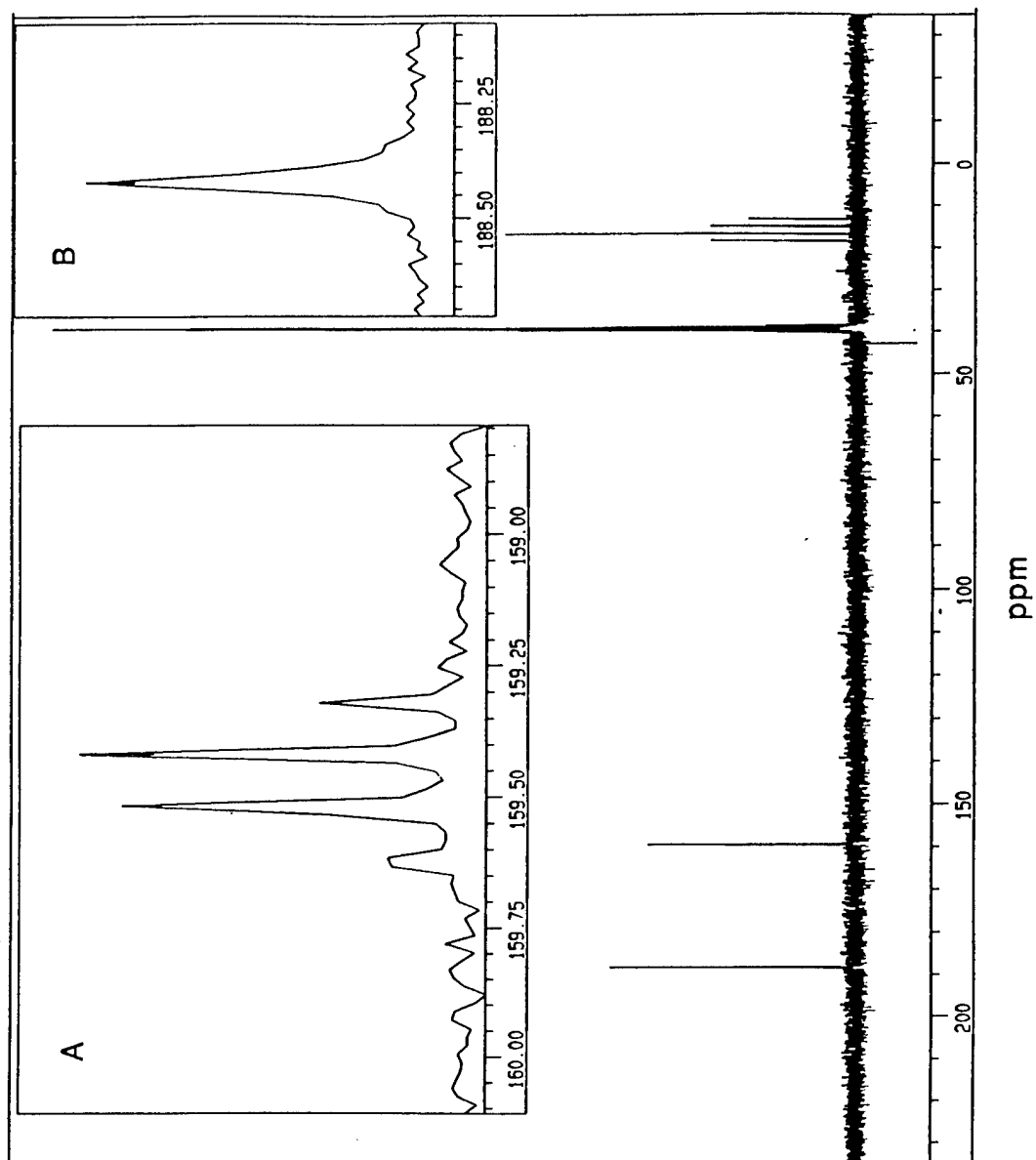
Figure 8: Raman (top) and IR absorbance (bottom) spectra of DMcT.

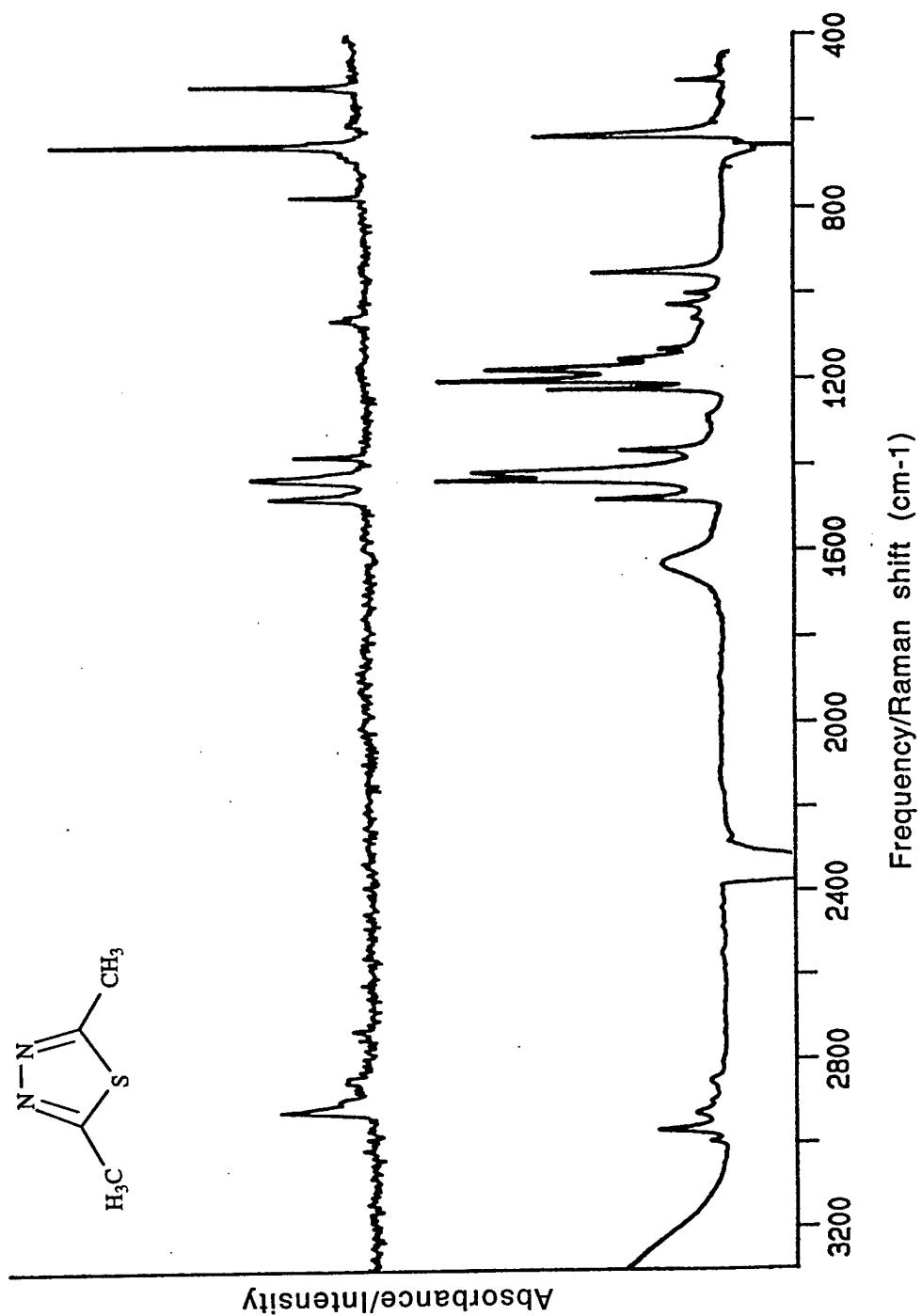
Figure 9: Raman (top) and IR absorbance (bottom) spectra of dimer DMcT.



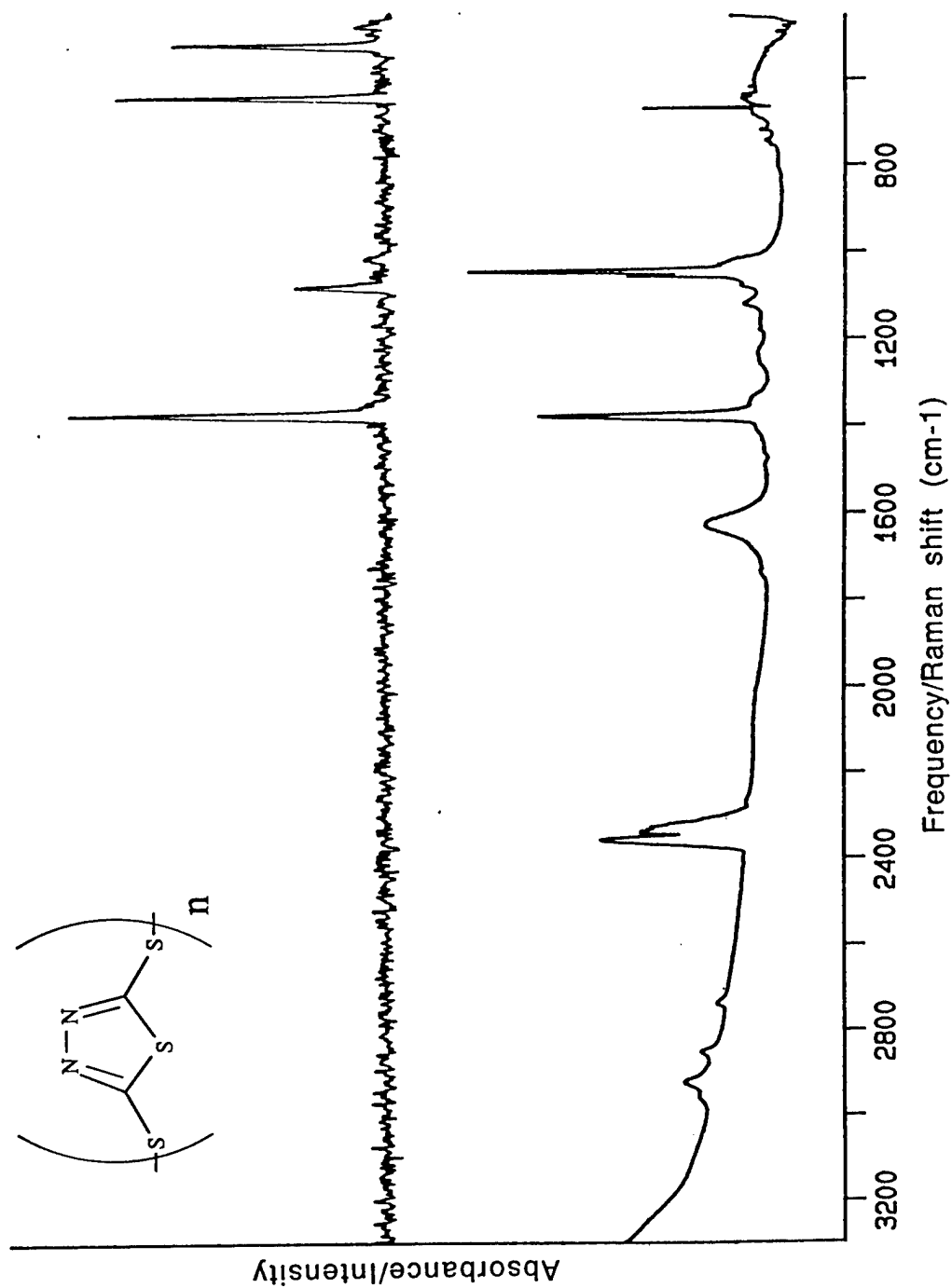
Pope, et.al. Figure 1a

Pope, et.al. Figure 11

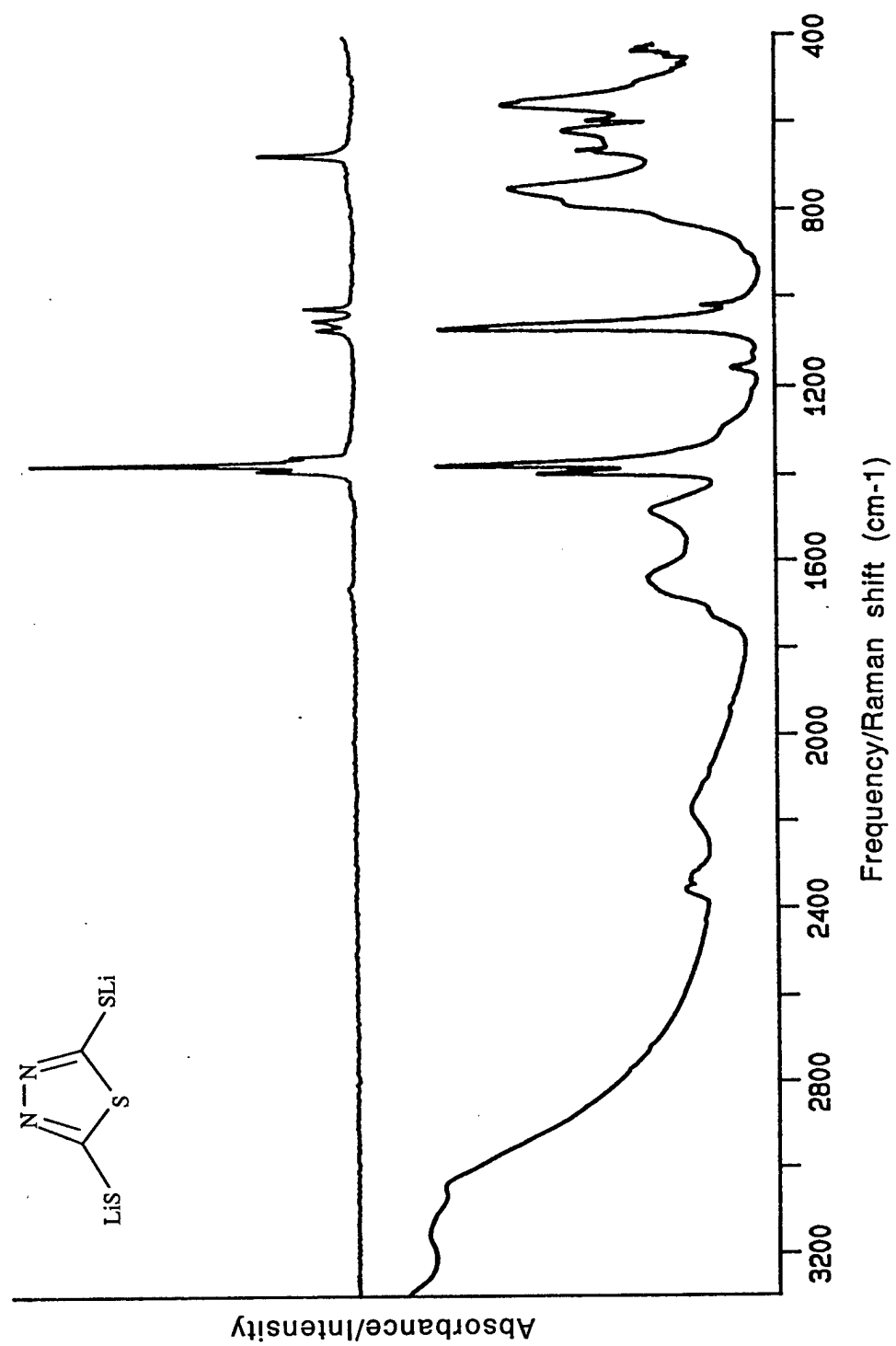




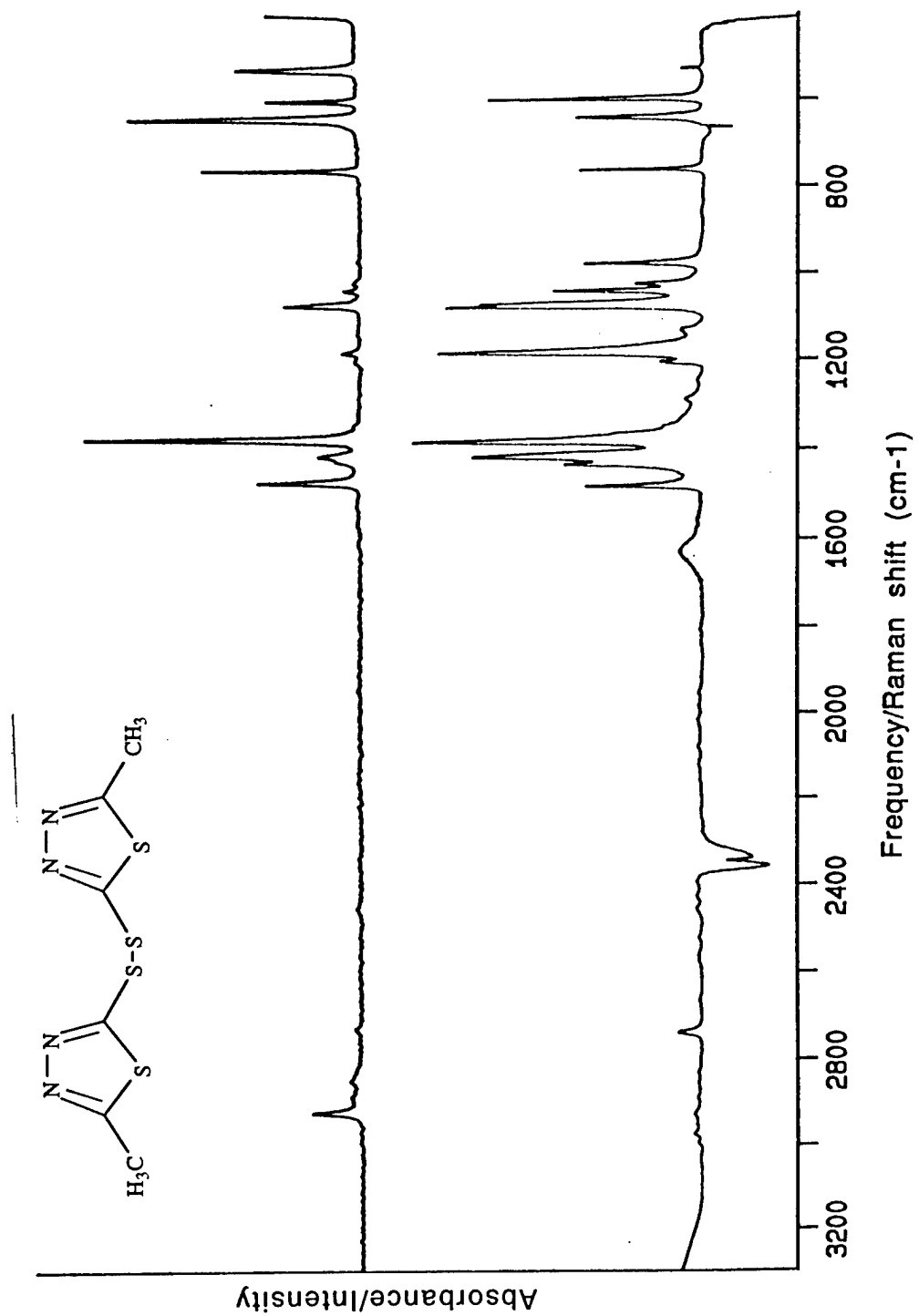
Pope, et. al. Figure.



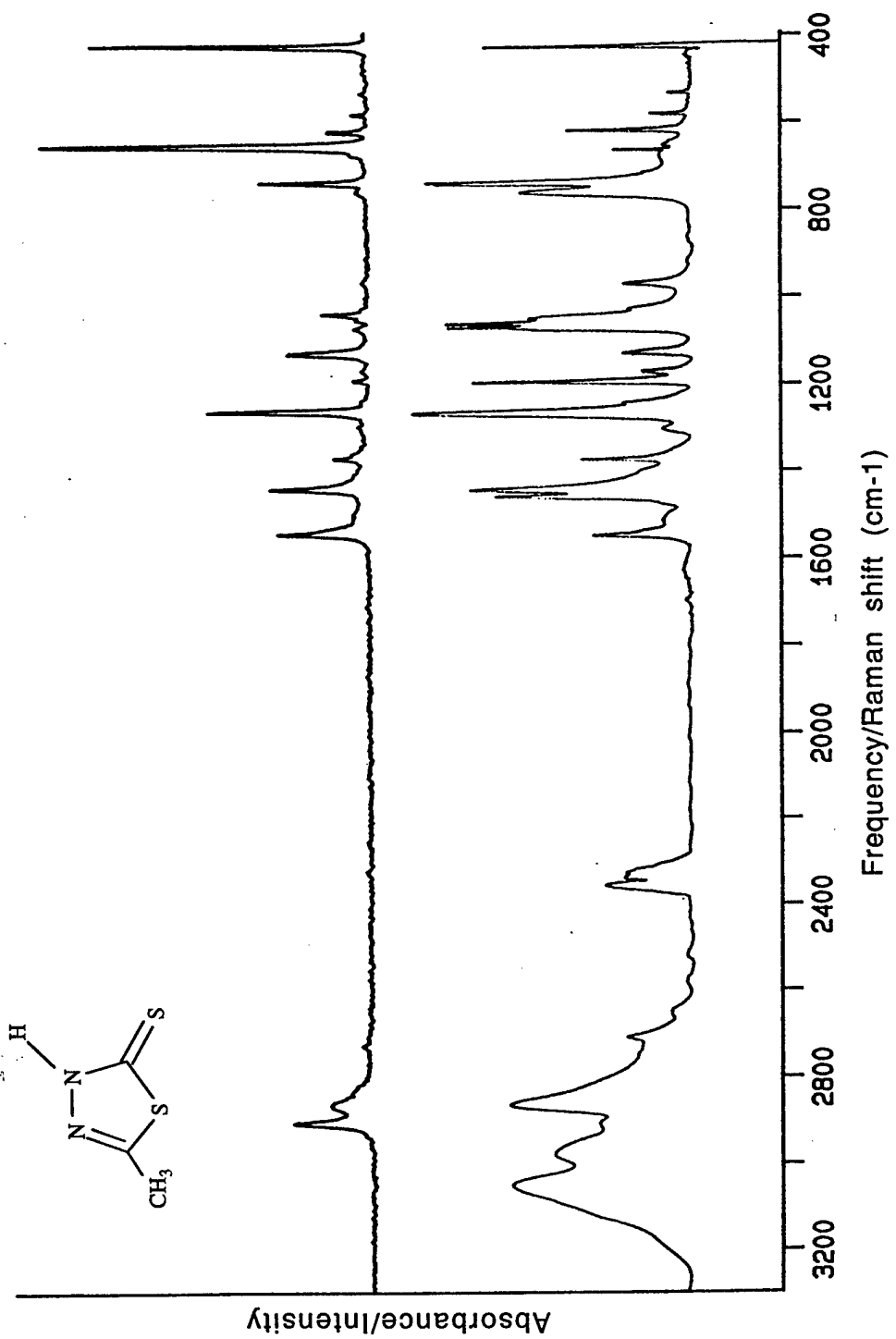
Pope, et.al. Figure 3



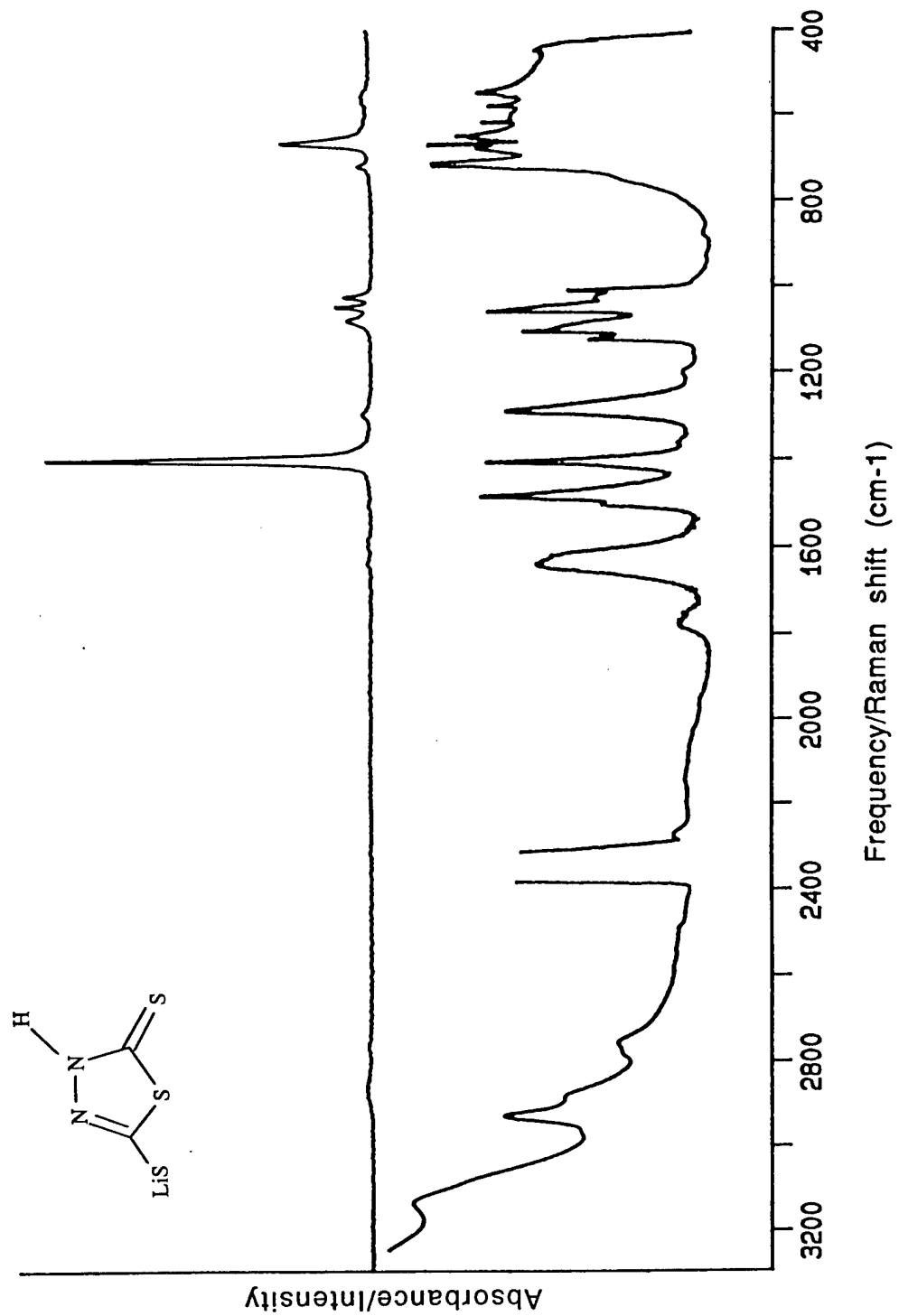
Pope, et.al. Figure 4



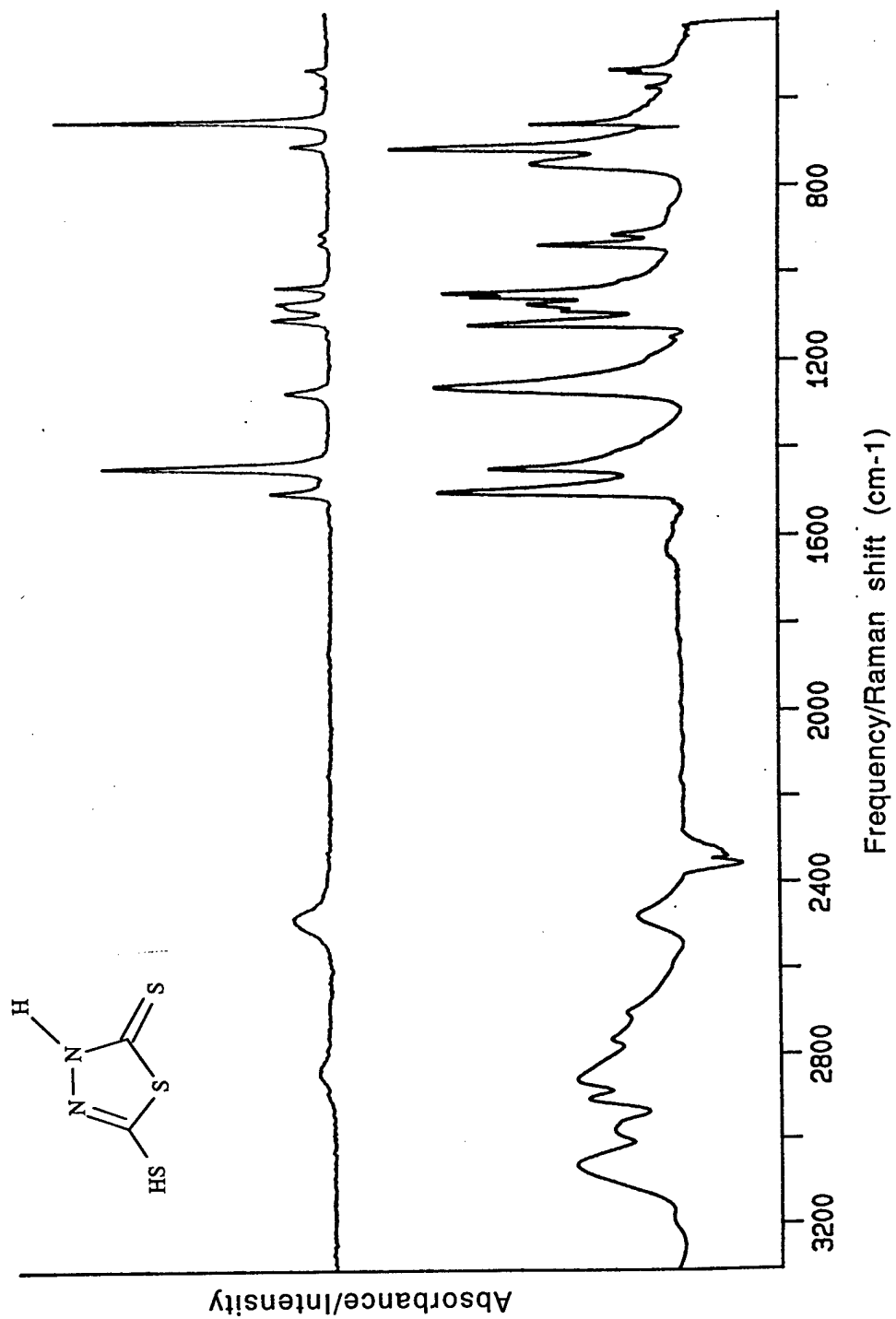
Pope, et. al. Figure 5



Pope, et.al. Figure 6



Pope, et. al. Figure 7



Pope, et. al. Figure 8

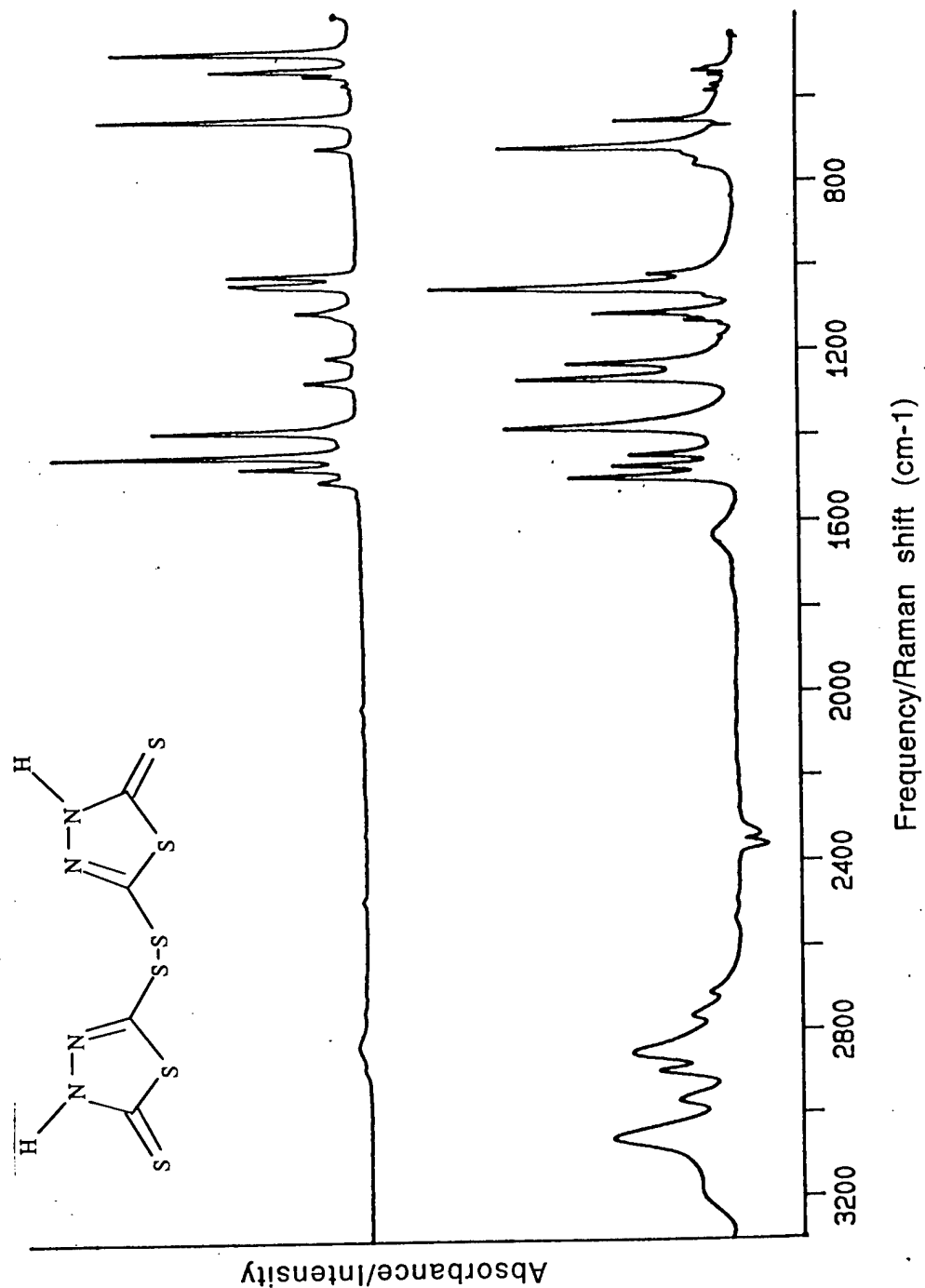


Fig. 1. IR spectrum of the compound.